

Electrical Conductive Surface Functionalization of Polycarbonate Parts with CNT Composite Films during Injection Molding

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Abstract

This study describes a reactive process to transfer an electrical conductive polycarbonate (PC) film onto the surface of bulk polycarbonate by an injection molding process using hyper branched poly (ethylenimine) (PEI). Due to a nucleophilic substitution reaction between the amino groups of the poly (ethylenimine) and the carbonate groups of the PC, a stable covalent crosslinking is established. The resulting conductive layer has an average thickness of about 3 - 7 µm and a surface roughness that depends on the roughness of the cavity. The lowest resulting electrical surface resistivity of the final injection molded part of $5.58 \cdot 10^4 \Omega$ per square is measured for a composites film loaded with 5 wt.% CNT. The crosslinking PEI layer has a thickness of about 50 nm, which equates with the hydrodynamic radius of a random PEI molecule with molecular weight of about 750.000 g·mol⁻¹. As a consequence, all PEI intermediate surface films remain completely on the PC parts.

Keywords

Injection Molding; Carbon Nanotubes; Surface Functionalization; Polymer Matrix Composites (Pmcs); Electrical Properties

Introduction

Electrically conductive polymer composites containing carbon nanotubes (CNTs) have gained high attention in the last years. The high aspect ratio and unique mechanical [1-5], electrical [6, 7] and thermal [8, 9] properties of the CNTs can be expected to result in outstanding composite properties when using the CNTs as filler material in melt mixed thermoplastic composites. Therefore, several applications like electromagnetically shielding [10, 11], gas barrier [12] or sensor materials [13-15] are currently under development. However, the full potential of CNT composites in industrial applications is not yet fully realized. This is due to the fact that a suitable dispersion and the distribution of the as-synthesized CNT agglomerates in the polymer matrix is quite difficult to achieve by melt mixing. Remaining primary CNT agglomerates have a negative effect especially on the mechanical composite properties but also on electrical conductivity. If nanotubes are restricted in agglomerates, they cannot contribute efficiently to the electrical network which is required to obtain electrical conductive composites. In order to achieve a good individualization of agglomerated nanotube materials, a variety of influencing factors must be considered. At first, the CNT structure itself (e.g., purity, functionalization, morphology and aspect ratio) and further the properties of the polymer matrix (e.g. viscosity, surface energy, and chemical structure) and certainly the processing conditions (e.g. mixing equipment, temperature, shear stresses e.g. influenced by screw configuration and screw speed, mixing time and the way of filler feeding) strongly influence the CNT dispersion [13, 16-22]. Caused by strong CNT intermolecular interactions (van der Waals and Coulomb interactions), there are tendencies to re-agglomerate into loose secondary agglomerates in the polymer melt upon storage or low shear [20, 23, 24]. Due to the high aspect ratio, a CNT orientation during injection molding [25] or fiber spinning [26] occurs which may delay or hinder electrical network formation. The filler orientation effect results in anisotropic mechanical properties and in a shift of the electrical percolation threshold (the lowest concentration at which an electrical network is formed) towards higher filler loadings which increase the cost of the final product. Hence, the final thermal processing step of composite shaping is crucial for the state of the CNT nano dispersion, distribution and orientation and therefore also for the resulting composite properties.

To prevent such problems by producing electrostatic dissipative or conductive materials, a localization of the CNT networks on the surface of the parts instead in the whole bulk appears to be ideal. In such a case, primary CNT agglomerates may not affect badly the overall mechanical properties of the whole injection molded part, which are dominated by the PC matrix. Thanks to this approach, the material cost can be reduced as only the part surface layer has to be modified. However, due to the further processing step additional costs could arise, which has to be offset. To achieve the desired electrical properties at the surface of a part, the CNT layer thickness has to be adjusted by retaining high CNT dispersion qualities.

Solution casting method, spin coating and spray coating are proper methods to form CNT composite films in the dimensions of several micrometers in thickness [27, 28]. An excellent adhesion between the electrical conductive CNT film and the injection molded part is essential for abrasion resistant surfaces. This can be achieved by chemical reactions, like for polycarbonate (PC) based composites by a thermal reactive linkage between the carbonate groups of the matrix and for example amine groups of poly(etherimines) (PEI) [29]. The nucleophilic substitution of the carbonate groups with amines under formation of urethane bonds [30-32] takes place in few seconds. This type of reaction provides the opportunity to transfer functional thin films directly during the injection molding process. Thereby, additional process steps can be avoided and the production time can be shortened.

In this study, this surface-reactive injection molding was used to combine an insulating PC matrix with a conductive PC-CNT composite film during the injection molding process. This principle is able to save expensive CNT material in comparison to completely filled CNT composites parts. Previous work [33] about the transfer of gold nanoparticles onto PC surfaces during injection molding was extended towards the possibility to transfer CNT composite layers on injection molded parts. Therefore, a thin two-layer film consisting of a chemical reactive PEI layer on top of a conductive PC-CNT composite was applied onto a supporting steel substrate. Subsequently, pure PC was injection molded onto this two-layer film system. The melt temperature of 300°C of the polymer in the cavity during the injection molding process initiates the chemical reaction between the polymer melt and PEI [34]. Consequently, a resistant linkage between the bulk PC and the PC-CNT composite film could be realized. Such formed parts are studied concerning the surface morphology and the electrical conductivity on the surface.

Experimental

Materials

For the composite preparation PC Makrolon PC 2600 (Bayer MaterialScience AG) with medium viscosity, a melt volume flow rate of $12 \text{ cm}^3 \cdot 10 \text{ min}^{-1}$ (ISO 1133; conditions 300 °C, 1.2 kg) was used. Commercially available multiwalled carbon nanotube (MWCNT) material was employed, namely Nanocyl™ NC7000 (Nanocyl S.A., Sambreville, Belgium). These nanotubes have a mean diameter of 10.0 nm and a mean nanotube length of 1341 nm [35] and according to the provider, the carbon purity is 90%. A reducing of the length during melt processing should be considered [35]. The bulk density of the CNT material is reported to be $66 \text{ kg} \cdot \text{m}^{-3}$ [36]. CNT composites with different CNT concentrations prepared using melt mixing by extrusion were dissolved in chloroform (ACS reagent, $\geq 99.8\%$, contains 0.5-1.0% ethanol as stabilizer), which was obtained from Sigma Aldrich. For injection molding a low viscosity PC Makrolon LED 2245 (Bayer MaterialScience AG) with high optical transmission, a melt volume flow rate of $34 \text{ cm}^3 \cdot 10 \text{ min}^{-1}$ (ISO 1133; conditions 300 °C, 1.2 kg) was used. Hyperbranched PEI with a molecular weight of $M_w=750.000 \text{ g} \cdot \text{mol}^{-1}$ (Sigma-Aldrich, 50 wt.% solution in water) was applied as the reactive modifier. Ethanol (absolute; $\geq 99.8\%$; Sigma-Aldrich) was used as solvent for the PEI coating solution.

Sample Preparation

The MWCNT composites were produced by melt mixing with an intermeshing twin-screw extruder ZE25 from KraussMaffei Berstorff GmbH (Germany). A masterbatch containing 7.5 wt.% CNT was produced and subsequently diluted to get composites with filler contents of 2 wt.%, 3 wt.%, and 5 wt.%. Both processing steps were performed using a rotation speed of 500 min^{-1} , a throughput of $5 \text{ kg} \cdot \text{h}^{-1}$, barrel temperature program between 280 - 260 °C, and a distributive screw configuration with a length to diameter ratio of 48 (similar to screw SC-5 in [37]). In the masterbatch preparation, the MWCNTs were fed gravimetrically in a side feeder attached at 14 D. The chosen extrusion conditions are based on previous optimization studies [37, 38]. Before extrusion, the PC was

vacuum dried at least for 4 h at 120°C.

The melt mixed MWCNT composites were dissolved in 10 ml chloroform using 0.1 g of 2 wt.%, 3 wt.% and 5 wt.% MWCNT/PC composites. The MWCNT were further dispersed by sonication with an ultrasonic device Hielscher UP400S (Hielscher Ultrasonics GmbH, 400W und 24 kHz) and 5 mm diameter sonotrode at 20 % amplitude for 40 seconds. Afterwards, a thin film was prepared using the solution casting method with 0.65 ml composite dispersion on a 5 cm diameter polished steel substrate (after removing the peel ply, the substrate was precleaned with ethanol, $R_a=0.049 \mu\text{m}$). Subsequently, these modified substrates were immersed in a solution of 1 wt.% PEI in ethanol using dip-coating. Finally, the coated substrates were mounted with magnetic holders in the mold cavity of the injection molding machine. Injection molding was performed using the BOY 22 A HV (Dr. Boy GmbH & Co. KG, Germany) with a clamping force of 220 kN and a screw diameter of 18 mm. After closing the mold, the PC melt (300°C) was injected with a velocity of $7.6 \text{ cm}^3 \cdot \text{s}^{-1}$ into the preheated round cavity (80°C) which has a diameter of 50 mm and thickness of 3 mm (with the sprue located in the center). When solidification and cooling are completed, the formed part was ejected and separated from the steel substrate whereby the original two-layer film was transferred onto the PC disk. For comparison, PC films without nanotubes were transferred in the same way. Overall, for each material combination, three injection molding transfers were performed.

Characterization Methods

1) MWCNT Dispersion

To quantify the state of the MWCNT macro dispersion of the melt mixed composites, of the solution-casted MWCNT films and of the MWCNT-polycarbonate surface layer on the injection molded plates, an Olympus BH2 microscope in transmission mode was used. The microscope was combined with a DP71 camera (Olympus Deutschland GmbH, Hamburg, Germany). Observations of the melt mixed MWCNT composites were performed on thin sections of 5 μm thickness prepared from extruded strands using a Leica RM 2055 microtome (Leica Microsystems GmbH, Wetzlar, Germany).

To investigate the dispersion of MWCNT on the part surfaces at the nanoscale, a scanning electron microscope (SEM) using an Ultra Plus Field Emission Gun Scanning Electron Microscope (FEG-SEM, Carl Zeiss AG, Oberkochen, Germany) was used in the charge contrast imaging mode. In this mode, only the nanotubes participating in the electrical conductive network are visualized. To investigate the interface between the surface layer and the PC part, transmission electron microscopy (TEM, LIBRA120, Carl Zeiss AG, Oberkochen, Germany) using an acceleration voltage of 120 kV was applied. These observations were done on ultrathin samples which were prepared with a thickness of about 80 nm using a Reichert Ultracut S Ultramicrotome (Leica Microsystems GmbH, Wetzlar, Germany) at room temperature with an oscillating diamond knife.

2) Surface Topography

Surface topography investigations were performed using the MicroGlider 600R (Fries Research & Technology GmbH, Bergisch Gladbach, Germany), equipped with a H2 300 μm Sensor, in a range of 1 mm x 1 mm. A chromatic distance measurement was applied to determine the topography and the layer thickness. The resolution of 1000 x 1000 measuring points with a measuring frequency of 1000 Hz was selected. Surface roughness values are given as the arithmetic mean roughness (R_a).

3) Film Adhesion Test

Mechanical stability and adhesion between the layers was measured with a peel test where a duct tape was stuck on the nanocomposite surface layer covering the diameter of the part. The duct tape was strongly pressed on the thin film and afterwards it was pulled off quickly in an angle of 90°. The adhesive strength of the used duct tape to the pure PC surface was about 0.3 N · mm⁻¹.

4) Electrical Measurements

The electrical surface resistivity of the CNT composite thin films on the steel substrates or on the injection molded parts was measured using a Loresta-GP MCP-T610 electrometer in combination with a 4-point ESP-probe (Mitsubishi Chemical Corporation, Japan, external source electrodes spacing 15 mm and measuring

electrodes spacing 5 mm). The ESP probe was set on different locations of the conductive surfaces and the results shown are mean values of 5 measurements.

Results and Discussion

Principle of Creating the Conductive Surface Layer

To create an electrically conductive nanotube surface by the reactive injection molding process, a reactive modifier is needed which is able to link the PC-CNT composite film with the bulk PC during the injection molding process. Hyper branched PEI is capable to crosslink these two PC components due to a nucleophilic substitution between amino and carbonate groups (see Figure 1). At 300°C, the formation of urethane bonds can take place in a few seconds. Therefore, a reactive bonding using PEI can be easily realized with a conventional injection molding device.

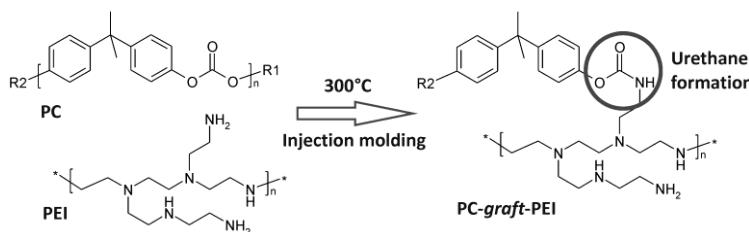


FIG. 1 CONVERSION OF THE CARBONATE GROUPS WITH AMINO GROUPS TO A URETHANE LINKAGE BETWEEN POLYCARBONATE AND PEI DURING INJECTION MOLDING

The principle of the transfer of the CNT composite film to the bulk polycarbonate surface is shown in Figure 2. In the first step, the PC-CNT composite was applied to the polished steel substrates by the solution-casting method. Afterwards, the substrates were coated with PEI by dip-coating. Subsequently, the PC-CNT composite film was transferred on the bulk polycarbonate surface during the reactive injection molding process. Consequently, the CNT composite film is covalently fixed on the surface of the injection molded part. The steel substrate is just a simplified model system for a cavity wall to demonstrate the principle of reactive injection molding. Alternatively, the film deposition on the steel substrate or on the cavity wall can be also done by spray coating.

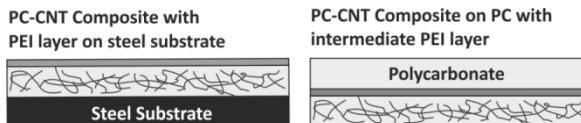


FIG. 2 PRINCIPLE OF THE TRANSFER OF THE PC-CNT COMPOSITE FILM TO THE BULK POLYCARBONATE DURING INJECTION MOLDING. THE PEI LAYER IS DRAWN IN DARK GREY. IT FORMS THE INTERMEDIATE LAYER AFTER INJECTION OF PC.

The PEI layer thickness is crucial for the peel strength of the thin films [39] onto the substrate. A too thin PEI layer does not offer enough reactive amino groups to ensure the formation of a sufficient number of covalent bonds with the polycarbonate surface. A very thick PEI layer leads to a cohesive failure within the PEI layer. Moreover, a high PEI layer thickness would hinder the heat conduction through the PEI layer interface during molding [40], hence the temperature would be insufficient to form covalent bonds. The reactions of PEI with PC were investigated in a previous paper [39] and it was demonstrated that high melt ($T_{melt} = 300^\circ\text{C}$) and mold ($T_{mold} = 80^\circ\text{C}$) temperatures are suitable for realizing a high adhesion between the PEI layer and PC. At such high temperatures, the thermal energy is sufficiently high to accelerate the urethane formation reaction.

Characterization of the CNT Dispersion and Film Morphology

First, within the PC-CNT composite film, a homogenous CNT dispersion in the PC matrix had to be established. Usually, CNT and PC and the organic solvent were mixed together and dispersed using ultra-sonic aid. According to Staudinger et al. [41], a distinctly improved dispersion quality and stability can be achieved by pre-dispersing the CNTs in a polymer melt by melt-mixing, followed by dissolving this premixture in an organic solvent using ultra-sonication. Thereby, in this study the melt-mixing masterbatch approach was used to produce a pre-dispersion of CNTs in PC composites with the expectation of the best possible dispersion state. This involved first the preparation of a 7.5 wt.% masterbatch which afterwards was diluted towards 2, 3, or 5 wt.% composites. The melt-mixed PC-CNT composites were nearly free of remaining CNT agglomerates (see Figure 3, A) illustrating that the dispersion strategy was successful. These well dispersed composites were dispersed in chloroform afterwards

using ultra-sonication to obtain dispersions with 1 wt.% of the corresponding PC-CNT composites. A moderate energy input (40 sec, 20 % amplitude) was applied to avoid additional possible CNT shortening. Afterwards, thin films were prepared by solution-casting the nanocomposite-chloroform dispersion on the steel substrates. During the film formation, the chloroform evaporated whereby the CNTs partly re-agglomerate (Figure 3, B).

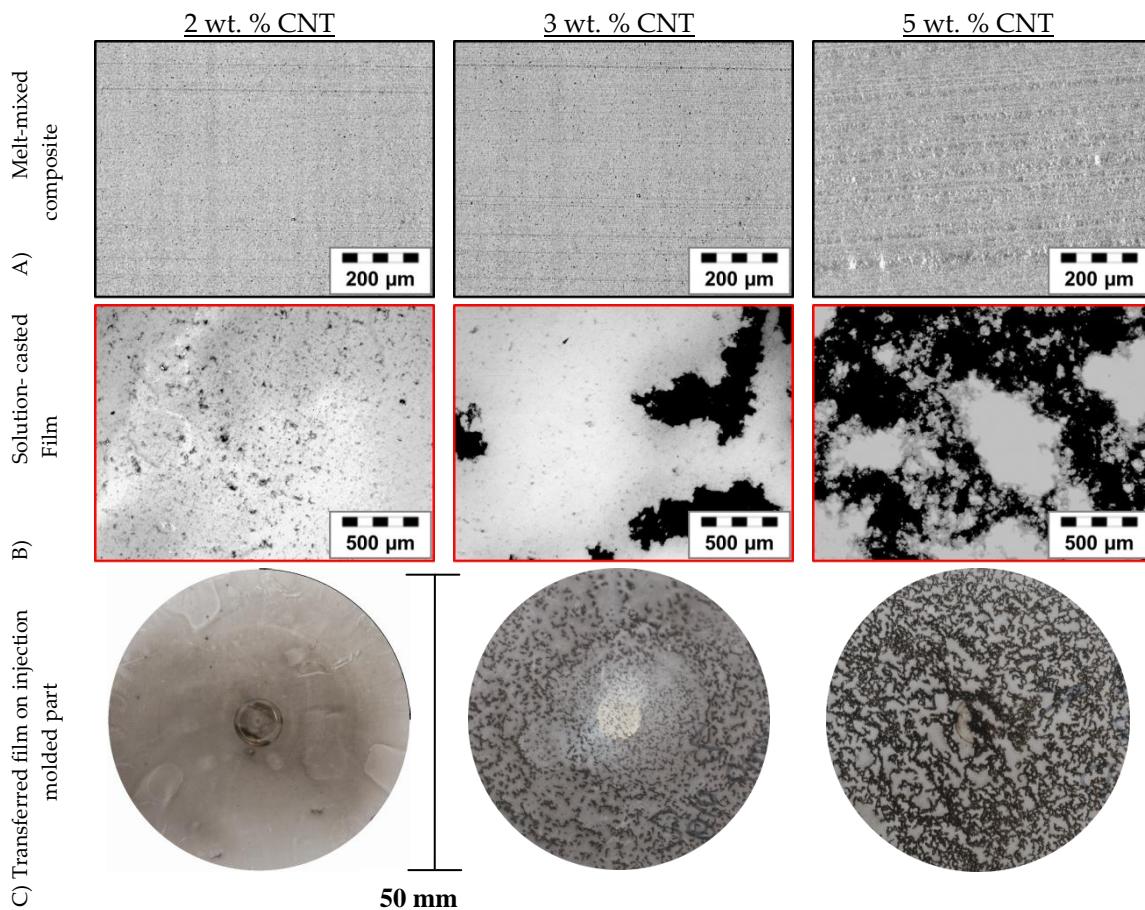
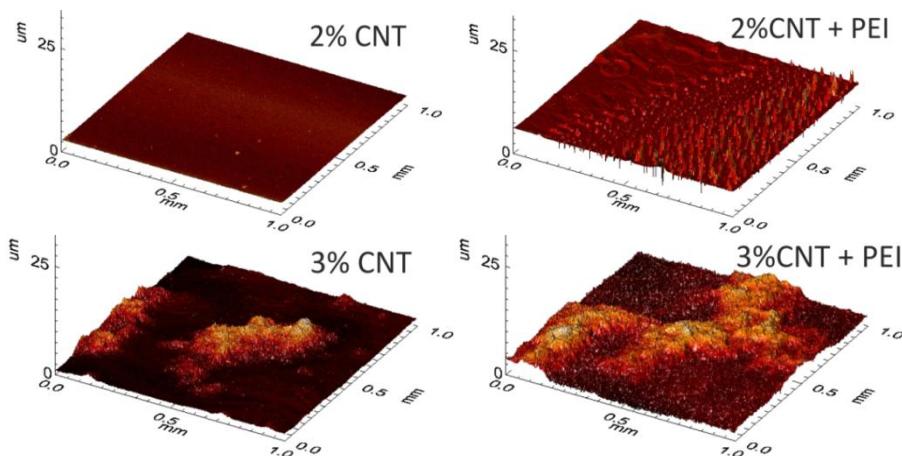


FIG. 3 CNT MACRO DISPERSION OF THE PC-CNT COMPOSITES OBSERVED WITH TRANSMISSION MICROSCOPY AFTER MELT MIXING. A: 5 μm THIN COMPOSITE SECTION, B: AFTER CASTING FROM SOLUTION 0.1 g in 10 ml CHCl_3 , 40 SEC ULTRA-SONIC TREATMENT, C: AFTER INJECTION MOLDING.

Even if the stabilizing effect of polycarbonate in chloroform on the stability of the CNT dispersion was shown by Staudinger et al. [41], obviously, the effect of PC chains adsorbed on CNTs was not fully applicable in our studies which may be due to the higher CNT concentrations. The CNT re-agglomeration in the chloroform dispersions was mainly observed when the CNT concentration in the composites was 3 wt.% or 5 wt.%. The dimensions of the formed aggregated structures were larger than the average thickness of the thin films (1.5-7 μm). Thereby, the surface roughness, measured using a MicroGlider, increased from 0.057 μm for 2 wt.% CNT sample to 0.490 μm and 0.851 μm for 3 and 5 wt.% loaded PC-CNT composites, respectively (Figure 4, left column).



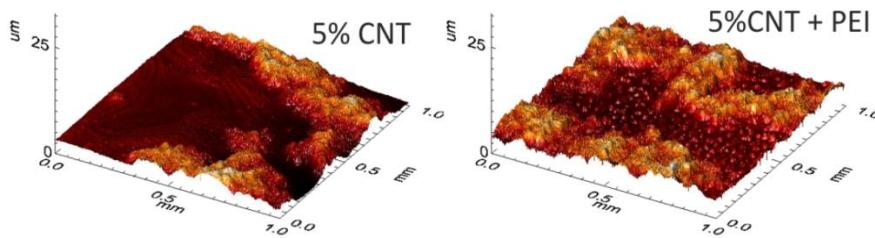


FIG. 4 ROUGHNESS (R_a) OF THE SOLUTION-CASTED PC-CNT NANOCOMPOSITE FILMS ON POLISHED STEEL, WITHOUT AND WITH APPLIED PEI DIP-COATING LAYER AT DIFFERENT CNT CONCENTRATIONS.

After the immersion of the polished steel-PC-CNT substrates in the ethanolic 1 wt.% PEI solution, small droplets of PEI were seen in the micrographs of the corresponding samples (Figure 4, right column). This indicated that PEI was not able to cover the whole PC-CNT composite surface as a homogeneous film. Therefore, the roughness value increased from $0.057 \mu\text{m}$ to $0.171 \mu\text{m}$ for the PEI-modified thin film with 2 wt.% CNT. The same effect could be observed for the film formation of PEI on the thin PC-CNT composite films with 3 wt.% and 5 wt.% CNT.

The PEI droplet formation during the ethanol evaporation process is based on the relatively low vapor pressure of ethanol. Due to the slow evaporation, the PEI molecules got carried away due to dewetting process and small PEI spots were formed. Furthermore, the dewetting processes were based on the relationship between the surface tension of PEI and PC. Obviously, the surface tension of hydrophobic PC $\sigma = 34.2 \text{ mN} \cdot \text{m}^{-1}$ [42] was too low to ensure a good wetting by the hydrophilic PEI ($\sigma = 40 \text{ mN} \cdot \text{m}^{-1}$).

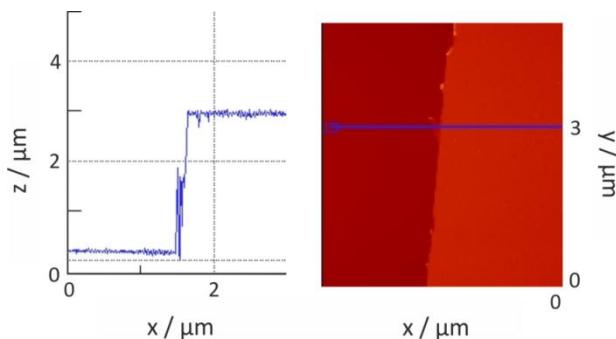


FIG. 5 TYPICAL RESULTS OF THE MICROGLIDER MEASUREMENTS TO OBTAIN THE FILM THICKNESS OF THE SOLUTION-CASTED PC-CNT COMPOSITE FILMS (EXAMPLE SHOWS 2WT.% CNT LOADING).

The average film thickness was obtained by MicroGlider measurements (Figure 5). The composite film with 2 wt.% CNT showing a rather smooth surface (see Figure 4) had an average thickness of about $3 \mu\text{m}$. The corresponding PEI droplets increased the roughness. The film thicknesses containing 3 and 5 wt.% CNT were not uniform but varied between $1.5 - 7 \mu\text{m}$. These variations were a result of the CNT agglomerates formed in the films.

Properties of the Injection Molded Parts

The steel substrate, covered with the thin layer of the PC-CNT composite with the (non-perfect) PEI layer on top, was mounted in the mold. The PC melt having a temperature of 300°C was injected into the mold against the mounted thin film-covered steel substrate. After solidification and cooling, the ejected part was separated from the steel substrate and investigated.

By optical inspection, no residues of the films were found on the substrates. Photographs of the final injection molded parts are shown in Figure 3, C illustrating that the state of the CNT dispersion and agglomeration in PC observed in the two-layer thin films did not change during the transfer from the substrate to the part. A melting of the thin two-layer films was not expected due to the low mold temperature and the fast cooling rate of the melt at the interface layer. Due to the layer inversion during injection molding, the thin film surface had now nearly the same roughness as the steel substrate (see Table 1).

In all samples using the PEI supported process, the nanocomposite films were bonded to the surface of the PC parts and could not be removed. The reference experiments performed without the application of the reactive PEI layer resulted in most cases in a partial remaining of the CNT composite film on the steel substrate. Moreover, the transferred part of the nanocomposite was just loosely bonded to the injection molded PC surface and could be removed easily. Therefore, it was concluded that the use of a reactive PEI layer supported the adhesion between the PC-CNT layer and the PC part very effectively, as it was intended.

TABLE 1 ROUGHNESS (R_a) OF THE TRANSFERRED PC FILMS WITH AND WITHOUT CNTS, MEASURED ON THE INJECTION MOLDED PART.

Sample	Roughness / μm *
Polished steel substrate without polymer film	0.049
Transferred PC film	0.068
Transferred PC 2 wt.% CNT film	0.082
Transferred PC 3 wt.% CNT film	0.373
Transferred PC 5 wt.% CNT film	0.231

* arithmetic mean roughness (R_a)

The adhesive strength of the bonded PC-CNT composite films was investigated by the peel test with a duct tape. All PEI intermediated PC-CNT composite films remained completely on the PC parts after the test. Consequently, the adhesive strength of the PC-CNT composites exceeded the adhesive strength of the duct tape to the PC surface.

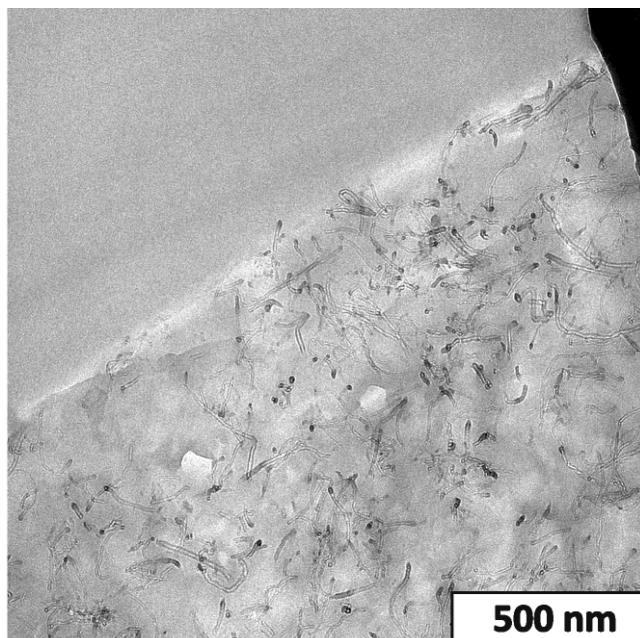


FIG. 6 TRANSMISSION ELECTRON MICROSCOPY IMAGE OF CROSS SECTION PERPENDICULAR TO THE INTERFACE BETWEEN THE PC PART AND THE PC-CNT COMPOSITE THIN FILM WITH 2WT.% CNT; CONNECTED VIA A THIN PEI LAYER.

Figure 6 shows transmission electron microscopy image of the boundary layer between the injection molded PC part and the PC-CNT composite film. The PEI droplets, which were visible on the PC-CNT composite film surface (see Figure 4, right column), formed a continuous layer during the injection molding process. Obviously, the process heat and the melt flow affected the PEI droplets, and a rather continuous film with even thickness was formed. The PEI layer thickness for the 2 wt.% CNT sample was about 50 nm, which similar to the size of a PEI molecule with a molecular weight of about 750.000 g·mol⁻¹. In addition, the excellent nanodispersion of the nanotubes near the interface is visible.

The electrical surface resistivity of the PC-CNT composite films before and after the transfer onto the PC parts is shown in Figure 7. Whereas the films with 2 wt.% CNT showed surface resistivities of $2.6 \cdot 10^6 \Omega \cdot \square^{-1}$ at higher CNT loading a further decrease of one ($3.9 \cdot 10^5 \Omega \cdot \square^{-1}$ for 3 wt.%) and two ($5.6 \cdot 10^4 \Omega \cdot \square^{-1}$ for 5 wt.%) orders of magnitude in surface resistivity were recognized. Such surface resistivity values are in the same range as for bulk melt-mixed PC-CNT injection molded composites. Villmow et al. reported for optimized injection molding parameters a measured surface resistivity of $10^6 \Omega \cdot \square^{-1}$ using 2 wt.% CNT and of $10^4 \Omega \cdot \square^{-1}$ using 5 wt.% CNT [25].

Interestingly, the surface resistivities were nearly unchanged after the transfer of the initial films on the PC part surfaces, again illustrating that the network structure could be transferred without significant changes. In the SEM images taken in the charge contrast imaging mode (Figure 8), a partially segregated percolated CNT network was observed for samples with 2 wt.% CNT content. In this mode, only the nanotubes participating in the electrical conductive network were visible. In comparison, the conducting CNT networks of the 3 wt.% and 5 wt.% PC-CNT composite films were denser and appeared to be more uniform over the hole sample in that scale, despite different

CNT dispersion states in more agglomerated or dispersed areas of these films.

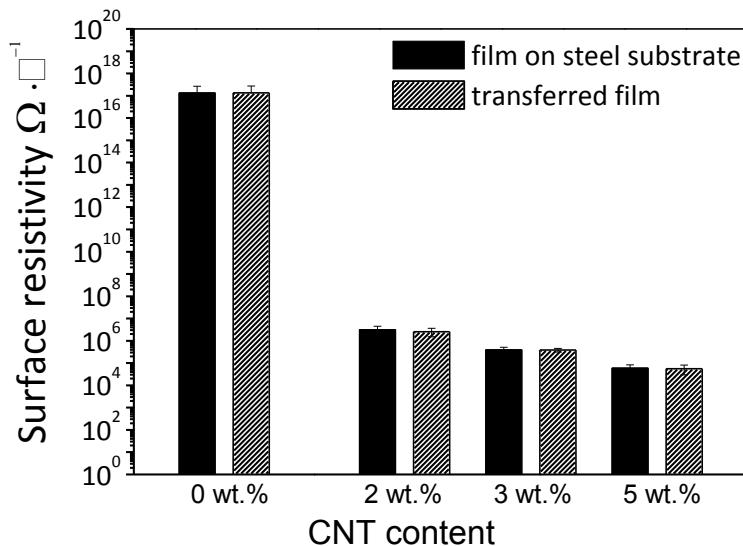


FIG. 7 ELECTRICAL SURFACE RESISTIVITIES OF THE PC-CNT COMPOSITE FILMS BEFORE AND AFTER INJECTION MOLDING TRANSFER.

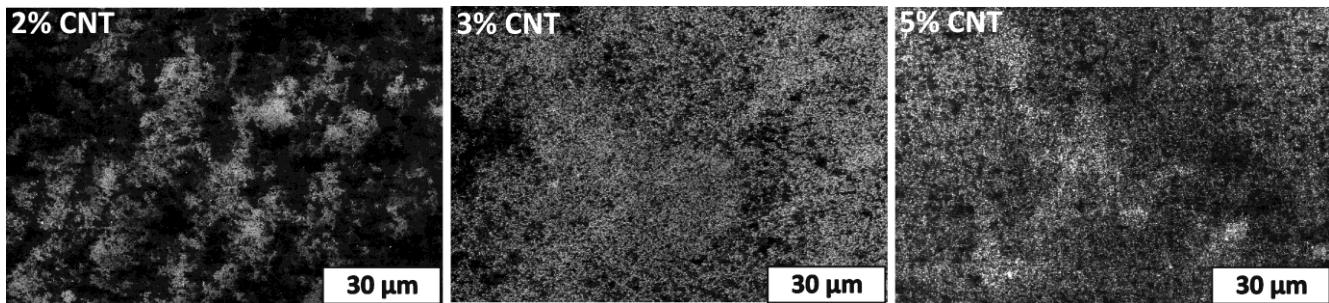


FIG. 8 CHARGE CONTRAST IMAGING (SEM) OF THE TRANSFERRED PC-CNT COMPOSITE FILMS.

Conclusions

In summary, this study showed a process to transfer an electrical conductive film on top of an injection-molded part. For this reactive injection molding process, a hyper branched poly(ethylenimine) was used to bind films of conductive multiwalled CNT- PC composites onto the PC bulk polymer surface. Due to a nucleophilic substitution reaction between the amino groups of the poly (ethylenimine) and the carbonate groups of the PC, a stable covalent crosslink between these two PC components was achieved. The polymer melt temperature of 300°C in the cavity during the injection molding process was sufficient to initiate this chemical reaction. The resulting conductive layers had average thicknesses of about 3 - 7 μm and a surface roughness which was dependent on the steel substrate roughness or, in industrial processing, the cavity roughness. The lowest resulting electrical surface resistivity of the final injection molding part was $5.6 \cdot 10^4 \Omega \cdot \square^{-1}$ when using a film containing 5 wt.% CNT composite. Thus, the CNT content of the whole PC part was approximately 0.01 wt.% due to the thin PC-CNT layer. The PC-CNT composite films were very thin so that they may not affect the overall mechanical properties of the whole injection molded part, which are dominated by the PC matrix. The application of mixed filler systems containing CNT and carbon black is proposed for reducing resistivity and realizing a uniformly dyed black surface, as it was shown for bulk composites [43, 44]. Finally, with the developed poly (ethylenimine)-mediated reactive injection molding process, electrically conductive surfaces can be easily realized on injection molded parts whereby the amount of the expensive CNT material can be significantly reduced as compared with bulk filled composites.

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REFERENCES

- [1] Demczyk, B. G., Wang, Y. M., Cumings, J., Hetman, M., Han, W., Zettl, A. and Ritchie, R. O. "Direct mechanical measurement of the tensile strength and elastic modulus of multiwalled carbon nanotubes." *Materials Science and Engineering: A* 334, 1-2 (2002): 173-178.
- [2] Lu, K. L., Lago, R. M., Chen, Y. K., Green, M. L. H., Harris, P. J. F. and Tsang, S. C. "Mechanical damage of carbon nanotubes by ultrasound." *Carbon* 34, 6 (1996): 814-816.
- [3] Peng, Bei, Locascio, Mark, Zapol, Peter, Li, Shuyou, Mielke, Steven L., Schatz, George C. and Espinosa, Horacio D. "Measurements of near-ultimate strength for multiwalled carbon nanotubes and irradiation-induced crosslinking improvements." *Nat Nano* 3, 10 (2008): 626-631.
- [4] Walters, D. A., Ericson, L. M., Casavant, M. J., Liu, J., Colbert, D. T., Smith, K. A. and Smalley, R. E. "Elastic strain of freely suspended single-wall carbon nanotube ropes." *Applied Physics Letters* 74, 25 (1999): 3803-3805.
- [5] Yu, Min-Feng, Lourie, Oleg, Dyer, Mark J., Moloni, Katerina, Kelly, Thomas F. and Ruoff, Rodney S. "Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes Under Tensile Load." 287, 5453 (2000): 637-640.
- [6] Ebbesen, T. W., Lezec, H. J., Hiura, H., Bennett, J. W., Ghaemi, H. F. and Thio, T. "Electrical conductivity of individual carbon nanotubes." *Nature* 382, 6586 (1996): 54-56.
- [7] Hong, Seunghun and Myung, Sung "Nanotube Electronics: A flexible approach to mobility." *Nat Nano* 2, 4 (2007): 207-208.
- [8] Pop, Eric, Mann, David, Wang, Qian, Goodson, Kenneth and Dai, Hongjie "Thermal Conductance of an Individual Single-Wall Carbon Nanotube above Room Temperature." *Nano Letters* 6, 1 (2005): 96-100.
- [9] Sun, Ke, Stroscio, Michael A. and Dutta, Mitra "Thermal conductivity of carbon nanotubes." *Journal of Applied Physics* 105, 7 (2009): -.
- [10] Huang, Yuan-Li, Yuen, Siu-Ming, Ma, Chen-Chi M., Chuang, Chia-Yi, Yu, Kuo-Chi, Teng, Chih-Chun, Tien, His-Wen, Chiu, Yie-Chan, Wu, Sheng-Yen, Liao, Shu-Hang and Weng, Fang-Bor "Morphological, electrical, electromagnetic interference (EMI) shielding, and tribological properties of functionalized multi-walled carbon nanotube/poly methyl methacrylate (PMMA) composites." *Composites Science and Technology* 69, 11-12 (2009): 1991-1996.
- [11] Thomassin, Jean-Michel, Huynen, Isabelle, Jerome, Robert and Detrembleur, Christophe "Functionalized polypropylenes as efficient dispersing agents for carbon nanotubes in a polypropylene matrix; application to electromagnetic interference (EMI) absorber materials." *Polymer* 51, 1 (2010): 115-121.
- [12] Ko, Jeong-Ho, Yoon, Choon Sup and Chang, Jin-Hae "Polypropylene nanocomposites with various functionalized-multiwalled nanotubes: thermomechanical properties, morphology, gas permeation, and optical transparency." *Journal of Polymer Science Part B: Polymer Physics* 49, 3 (2011): 244-254.
- [13] Kasaliwal, G. R., Pegel, Sven, Göldel, Andreas, Pötschke, Petra and Heinrich, Gert "Analysis of agglomerate dispersion mechanisms of multiwalled carbon nanotubes during melt mixing in polycarbonate." *Polymer* 51, 12 (2010): 2708-2720.
- [14] Villmow, Tobias, Pegel, Sven, Pötschke, Petra and Heinrich, Gert "Polymer/carbon nanotube composites for liquid sensing: Model for electrical response characteristics." *Polymer* 52, 10 (2011): 2276-2285.
- [15] Bautista-Quijano, J. R., Avilés, F., Aguilar, J. O. and Tapia, A. "Strain sensing capabilities of a piezoresistive MWCNT-polysulfone film." *Sensors and Actuators A: Physical* 159, 2 (2010): 135-140.
- [16] Andrews, Rodney, Jacques, David, Minot, Mickael and Rantell, Terry "Fabrication of Carbon Multiwall Nanotube/Polymer Composites by Shear Mixing." *Macromolecular Materials and Engineering* 287, 6 (2002): 395-403.
- [17] Kasaliwal, G., Göldel, A. and Pötschke, P. "Influence of Processing Conditions in Small-Scale Melt Mixing and Compression Molding on the Resistivity and Morphology of Polycarbonate-MWNT Composites." *Journal of Applied Polymer Science* 112, 6 (2009): 3494-3509.
- [18] Krause, B., Pötschke, P. and Häussler, L. "Influence of small scale melt mixing conditions on electrical resistivity of carbon nanotube-polyamide composites." *Composites Science and Technology* 69, 10 (2009): 1505-1515.

- [19] Müller, Michael Thomas, Krause, Beate, Kretzschmar, Bernd and Pötschke, Petra "Influence of feeding conditions in twin-screw extrusion of PP/MWCNT composites on electrical and mechanical properties." *Composites Science and Technology* 71, 13 (2011): 1535-1542.
- [20] Pegel, S., Pötschke, P., Petzold, G., Alig, I., Dudkin, S. M. and Lellinger, D. "Dispersion, agglomeration, and network formation of multiwalled carbon nanotubes in polycarbonate melts." *Polymer* 49, 4 (2008): 974-984.
- [21] Pötschke, Petra, Dudkin, Sergej M. and Alig, Ingo "Dielectric spectroscopy on melt processed polycarbonate-multiwalled carbon nanotube composites." *Polymer* 44, 17 (2003): 5023-5030.
- [22] Socher, Robert, Krause, Beate, Müller, Michael T., Boldt, Regine and Pötschke, Petra "The influence of matrix viscosity on MWCNT dispersion and electrical properties in different thermoplastic nanocomposites." *Polymer* 53, 2 (2012): 495-504.
- [23] Alig, I., Skipa, T., Engel, M., Lellinger, D., Pegel, S. and Pötschke, P. "Electrical conductivity recovery in carbon nanotube-polymer composites after transient shear." *physica status solidi (b)* 244, 11 (2007): 4223-4226.
- [24] Yoon, Howon, Okamoto, Kenzo, Umishita, Kazunori and Yamaguchi, Masayuki "Development of conductive network of multiwalled carbon nanotubes in polycarbonate melt." *Polymer Composites* 32, 1: 97-102.
- [25] Villmow, Tobias, Pegel, Sven, Pötschke, Petra and Wagenknecht, Udo "Influence of injection molding parameters on the electrical resistivity of polycarbonate filled with multi-walled carbon nanotubes." *Composites Science and Technology* 68, 3-4 (2008): 777-789.
- [26] Pötschke, Petra, Andres, Timo, Villmow, Tobias, Pegel, Sven, Brünig, Harald, Kobashi, Kazufumi, Fischer, Dieter and Häussler, Liane "Liquid sensing properties of fibres prepared by melt spinning from poly(lactic acid) containing multi-walled carbon nanotubes." *Composites Science and Technology* 70, 2 (2010): 343-349.
- [27] Pradhan, Basudev, Kohlmeyer, Ryan R and Chen, Jian "Fabrication of in-plane aligned carbon nanotube-polymer composite thin films." *Carbon* 48, 1 (2010): 217-222.
- [28] Safadi, B., Andrews, R. and Grulke, E. A. "Multiwalled carbon nanotube polymer composites: Synthesis and characterization of thin films." *Journal of Applied Polymer Science* 84, 14 (2002): 2660-2669.
- [29] Härtig, Thomas, Nagel, Jürgen and Gehde, Michael "Material Bonding: Process-Integrated Surface Modification During Injection Molding." *Kunststoffe International* 2010, 01 (2010): 31-35.
- [30] Zimmerer, Cordelia, Heinrich, Gert, Wolff-Fabris, Frederik, Koch, Edmund and Steiner, Gerald "Chemical reactions between poly(carbonate) and poly(vinyl amine) thermally induced by a high magnetic field pulse." *Polymer* 54, 25 (2013): 6732-6738.
- [31] Caldwell, J. R. and Jackson, W. J. "Surface treatment of polycarbonate films with amines." *Journal of Polymer Science Part C: Polymer Symposia* 24, 1 (1968): 15-23.
- [32] Dyer, Elizabeth and Scott, Harvey "The Preparation of Polymeric and Cyclic Urethans and Ureas from Ethylene Carbonate and Amines." *Journal of the American Chemical Society* 79, 3 (1957): 672-675.
- [33] Nagel, Jürgen, Chunsod, Petchara, Zimmerer, Cordelia, Simon, Frank, Janke, Andreas and Heinrich, Gert "Immobilization of gold nanoparticles on a polycarbonate surface layer during molding." *Materials Chemistry and Physics* 129, 1-2 (2011): 599-604.
- [34] Nagel, J., Bräuer, M., Hupfer, B., Grundke, K., Schwarz, S. and Lehmann, D. "Investigations on the reactive surface modification of polycarbonate by surface-reactive injection molding." *Journal of Applied Polymer Science* 93, 3 (2004): 1186-1191.
- [35] Castillo, Frank Yepez, Socher, Robert, Krause, Beate, Headrick, Robert, Grady, Brian P., Prada-Silvy, Ricardo and Pötschke, Petra "Electrical, mechanical, and glass transition behavior of polycarbonate-based nanocomposites with different multi-walled carbon nanotubes." *Polymer* 52, 17 (2011): 3835-3845.
- [36] Krause, Beate, Mende, Mandy, Pötschke, Petra and Petzold, Gudrun "Dispersability and particle size distribution of CNTs in an aqueous surfactant dispersion as a function of ultrasonic treatment time." *Carbon* 48, 10 (2010): 2746-2754.

[37] Villmow, Tobias, Kretzschmar, Bernd and Pötschke, Petra "Influence of screw configuration, residence time, and specific mechanical energy in twin-screw extrusion of polycaprolactone/multi-walled carbon nanotube composites." *Composites Science and Technology* 70, 14 (2010): 2045-2055.

[38] Villmow, Tobias, Pötschke, Petra, Pegel, Sven, Häussler, Liane and Kretzschmar, Bernd "Influence of twin-screw extrusion conditions on the dispersion of multi-walled carbon nanotubes in a poly(lactic acid) matrix." *Polymer* 49, 16 (2008): 3500-3509.

[39] Härtig, T., Nagel, J., Lehmann, D. and Heinrich, G. "Process-integrated surface modification during injection molding." *Kunststoffe international : magazine for plastics ; official voice of German Plastics Associations*, (2010): 31-35.

[40] Nagel, Jürgen and Heinrich, Gert "Temperature transitions on the surface of a thermoplastic melt during injection moulding and its use for chemical reactions." *International Journal of Heat and Mass Transfer* 55, 23–24 (2012): 6890-6896.

[41] Staudinger, Ulrike, Krause, Beate, Steinbach, Christine, Pötschke, Petra and Voit, Brigitte "Dispersability of multiwalled carbon nanotubes in polycarbonate-chloroform solutions." *Polymer* 55, 24 (2014): 6335-6344.

[42] "Solid surface energy data (SFE) for common polymers." June 2015, 2015. <http://www.surface-tension.de/solid-surface-energy.htm>

[43] Socher, Robert, Krause, Beate, Hermasch, Sylvia, Wursche, Roland and Pötschke, Petra "Electrical and thermal properties of polyamide 12 composites with hybrid fillers systems of multiwalled carbon nanotubes and carbon black." *Composites Science and Technology* 71, 8 (2011): 1053-1059.

[44] Hiliarus, K., Lellinger, D., Alig, I., Villmow, T., Pegel, S. and Pötschke, P. "Influence of shear deformation on the electrical and rheological properties of combined filler networks in polymer melts: Carbon nanotubes and carbon black in polycarbonate." *Polymer* 54, 21 (2013): 5865-5874.

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